Novel anion binding selectivity trends exhibited by new dinuclear rhenium(I), ruthenium(II) and osmium(II) bipyridyl cleft-type receptors

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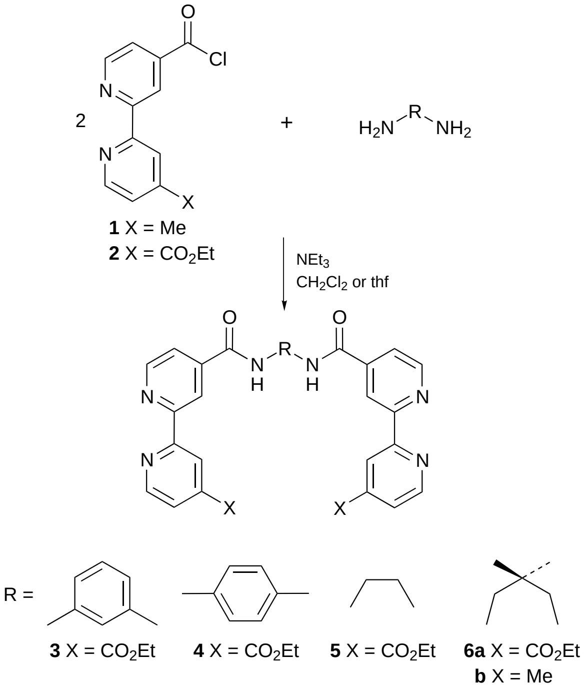
Novel dinuclear rhenium(I), ruthenium(II) and osmium(II) bipyridyl cleft-type receptor systems exhibit remarkable selectivity for dihydrogenphosphate over halide anions dictated by the nature of the bridging linkage and the transition-metal Lewis-acidic centre.

Anions are of crucial importance in many essential chemical and biochemical processes and therefore their binding and recognition is presently the subject of intensive research.[1] To date, a number of research groups have designed and synthesised anion binding reagents that use either favourable hydrogen-bonding interactions alone,[2,3] or hydrogen-bonding interactions in conjunction with electrostatic forces[4–6] to coordinate and, in some instances, sense anions. Examples of the latter which have been particularly successful in this respect are amide containing cobaltocenium[7,8] and ruthenium(II) polypyridyl molecules.[9–11] In an effort to enhance selective anion recognition through the design of new cooperative polymetallic Lewis-acidic systems, we report here the synthesis of novel dinuclear transition-metal bipyridyl, cleft-type receptors whose remarkable selectivity for the dihydrogenphosphate anion over halide anions is profoundly influenced by the nature of the bridging linkage, and the electronic character of the transition-metal Lewis-acidic centre.

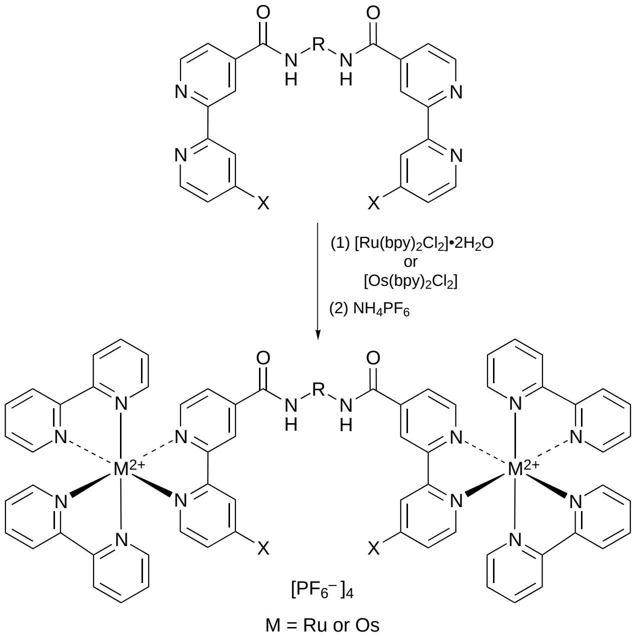
The reaction of 4-carboxy-4′-methyl-2,2′-bipyridine[12] or 4-carbonyl-4′-ethoxycarbonyl-2,2′-bipyridine[13] with thionyl chloride afforded the acid chlorides **1** and **2** respectively in quantitative yields. The condensation of 2 equiv. of **1** or **2** with 1 equiv. of diamine in dichloromethane solution afforded the new ‘cleft’-type bipyridyl (bpy) ligands **3–6** in excellent yields (Scheme 1). The free ligands were chelated to the positively charged $[M(bpy)_2]^{2+}$ fragment (M = Ru, Os) unit by reaction with either 2 equiv. of *cis*-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$[14] or *cis*-$[Os(bpy)_2Cl_2]$[15] in ethanol–water–acetic acid. The mixed ruthenium–osmium receptor, Ru–**6b**–Os, was prepared by reaction of ligand **6b** with 1 equiv. of *cis*-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$, followed by 1 equiv. of *cis*-$[Os(bpy)_2Cl_2]$. The crude products were purified by column chromatography on Sephadex LH-20 and converted to the hexafluorophosphate salts with an excess of aqueous NH_4PF_6 (Scheme 2). The rhenium(I) receptor, Re–**6b**–Re, was prepared by reaction of the free ligand **6b** with 2 equiv. of $[Re(CO)_5Br]$ in thf and purified by recrystallisation from acetone–diethyl ether (Scheme 3).‡

Proton NMR titration experiments with Cl^- and $H_2PO_4^-$ anions were carried out in $(CD_3)_2SO$ solution and revealed significant downfield shifts in the receptors’ amide and 3,3′-bpy protons. For example, the amide protons of Ru–**6b**–Ru were perturbed by 0.93 ppm and the 3,3′-bpy protons by 0.84 ppm after the addition of an excess of tetrabutylammonium dihydrogenphosphate. In all cases the resulting titration curves (for example, Fig. 1) suggest complexes with a 1 : 1 receptor : anion stoichiometry are formed in solution. Stability constants were calculated from the titration data using the EQNMR computer program[16] and the values are presented in Table 1.§

Clearly the nature of the bridging linkage has a dramatic influence on the anion binding strength and selectivity these dinuclear cleft-type receptors display. Of particular note is the

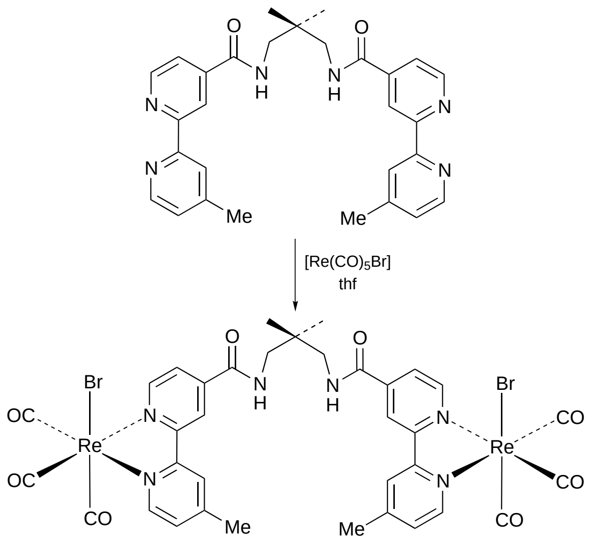


Scheme 1



Scheme 2

remarkable increase in the magnitude of stability constant of $H_2PO_4^-$ that results from simply altering the linkage from *m*-phenylene Ru–**3**–Ru (K = 55 M^{-1}) to *p*-phenylene Ru–**4**–Ru (K = 4320 M^{-1}), with the halide stability constant values remaining virtually unchanged. In addition, whereas the ethyl-bridged receptor Ru–**5**–Ru forms an extremely weak complex with $H_2PO_4^-$ and is Cl^- selective, the 2,2′-dimethyl-1,3-propane-bridged analogue, Ru–**6a**–Ru forms an extremely strong and selective complex with $H_2PO_4^-$. Comparing Ru–**6a**–Ru and Ru–**6b**–Ru, it is also of interest to note there is a significant 4′-bipyridyl substituent effect, with $H_2PO_4^-$ anions favouring the ester containing receptor and chloride the methyl containing one.



Scheme 3

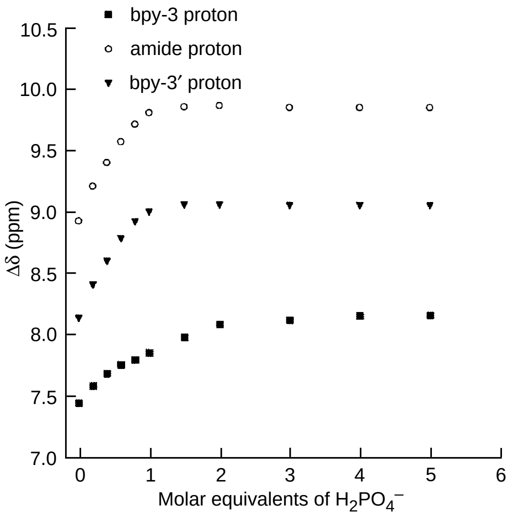


Fig. 1 ^1H NMR titration curve of Ru–**6b**–Ru with $NBu_4H_2PO_4$ in $(CD_3)_2SO$

Table 1 Stability constant data for dinuclear cleft-anion receptors in $(CD_3)_2SO$

Receptor	K (Cl^-)[a,b]/ M^{-1}	K (Br^-)[a,b]/ M^{-1}	K ($H_2PO_4^-$)[a,b]/ M^{-1}
Ru–**3**–Ru	25	45	55
Ru–**4**–Ru	55	40	4 320
Ru–**5**–Ru	70	60	10
Ru–**6a**–Ru	245	170	19 700
Re–**6b**–Re	120	—[c]	1 820
Ru–**6b**–Ru	310	220	15 480
Ru–**6b**–Os	440	—[c]	22 150
Os–**6b**–Os	825	—[c]	> 30 000

[a] Average for amide and bpy protons. [b] Errors estimated to be < 10%. [c] Not calculated.

Table 1 also demonstrates that the nature of the bipyridyl-coordinated transition-metal centre strikingly dictates the strength and degree of anion recognition selectivity. With both $H_2PO_4^-$ and Cl^- anionic guest species the stability constants increase in magnitude in the order Re–**6b**–Re < Ru–**6b**–Ru < Ru–**6b**–Os < Os–**6b**–Os. From electrostatic considerations it is perhaps not surprising the neutral bis-rhenium(i) receptor forms the relatively weaker anion complexes. However, what is unexpected is the dramatic increase in magnitude of stability constant for the osmium-containing receptors, especially in respect to $H_2PO_4^-$ complexation. This observation suggests the $(bpy)_2Os^{2+}$ moiety is a particularly efficient Lewis-acidic centre to incorporate into this new cleft-type class of transition-metal bipyridyl amide anion receptor.

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Footnotes

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‡ All new compounds were fully characterised by elemental analysis, ^1H and ^{13}C NMR and FABMS.

¶ The addition of chloride or dihydrogenphosphate anions to $(CD_3)_2SO$ solutions of $[M(bpy)_3)][PF_6]_2$ (M = Ru, Os) had no effect on the ^1H NMR spectrum. The metal-free bipyridyl ligands exhibited extremely weak and insignificant interactions with both chloride and dihydrogenphosphate anions in $(CD_3)_2SO$.

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